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Environmental Toxicology and Chemistry, Vol. 26, No. 9, pp. 1940–1948, 2007

Printed in the USA
0730-7268/07 $12.00 + .00

AVAILABILITY OF POLYCHLORINATED BIPHENYLS IN FIELD-CONTAMINATED SEDIMENT

JING YOU,† PETER F. LANDRUM,‡ TRICIA A. TRIMBLE,† and MICHAEL J. LYDY*†
†Fisheries and Illinois Aquaculture Center and Department of Zoology, 171 Life Science II, Southern Illinois University, Carbondale, Illinois 62901, USA
‡Great Lakes Environmental Research Laboratory, National Oceanic and Atmospheric Administration, 2205 Commonwealth Boulevard, Ann Arbor, Michigan 48105, USA

(*Received* 12 *January* 2007; *Accepted* 10 *April* 2007)

Abstract—Two chemical approaches, Tenax extraction and matrix solid phase microextraction (matrix-SPME), were evaluated as surrogates to estimate bioavailability of polychlorinated biphenyls (PCBs) from field-contaminated sediment. Aroclor 1254 was the primary contaminant found in sediment from Crab Orchard Lake in Marion, Illinois, USA, and a total of 18 PCB congeners were selected for study. Bioaccumulation was determined by exposing the freshwater oligochaete, *Lumbriculus variegatus*, to the sediment for 28 d. Differences in the rapidly desorbing fraction of PCBs and fraction desorbed within 6 h, defined by Tenax extraction, accounted for 39 and 31% of the differences among biota-sediment accumulation factor values, respectively. A better relationship (r^2 = 0.95) was found between the oligochaete PCB body residues and the concentration of PCBs in the rapidly desorbing fraction of sediment. The degree of chlorination and planarity of the PCB congeners affected both desorption and bioaccumulation. The higher chlorine substituted and planar PCBs showed less chemical and biological availability, due to their stronger sorption to sediment, compared to the lower chlorinated and nonplanar PCBs. Accumulation of PCBs by *L. variegatus* correlated well (r^2 = 0.88) with matrix-SPME fiber concentrations. The ratio of measured body residue to estimated body residue from the pore water concentration measured by matrix-SPME ranged from 0.4 to 1.3 with an average of 0.9. Overall, both Tenax and matrix-SPME approaches were useful surrogates of bioaccumulation for a field-contaminated sediment.

Keywords—Tenax extraction Matrix solid phase microextraction Field-contaminated sediment Bioaccumulation Polychlorinated biphenyl planarity

INTRODUCTION

Two chemical approaches have been proposed to estimate the bioavailable fraction of hydrophobic organic contaminants (HOCs) in sediment. The first approach determines the fraction of contaminant in the rapidly desorbing pool by measuring HOC desorption from sediment using Tenax beads (Alltech, Deerfield, IL, USA) [1]. Briefly, Tenax beads are added to a sediment water suspension and replaced periodically throughout the study. Tenax beads serve as an infinite sink quickly adsorbing all HOCs desorbed to the water. By removing the beads at timed intervals, desorption curves can be determined, and the rapid and slow pools of HOCs can be calculated [1].

Previous studies using Tenax beads to calculate the rapidly desorbing fraction (F_{rap}) have determined that both the entire contaminant–sediment desorption curve [1], and specific points along the curve (e.g., 6 h) may adequately describe F_{rap} [2]. Studies using the Tenax approach also have found that the size of F_{rap} was related to the contaminant contact time with the sediment [1]. In addition, a few studies have compared Tenax desorption to bioaccumulation. For example, biota-sediment accumulation factor (BSAF) values for polycyclic aromatic hydrocarbons (PAHs) in marine amphipods correlated well with F_{rap} [3]. Likewise, this approach explained a great deal of the variability in the BSAF values of several HOCs using oligochaetes [4,5]. This approach did not explain an observed decrease in BSAF values of tetrachlorobiphenyl (a polychlorinated biphenyl [PCB] congener) with increasing sediment concentration [6]. This variation was better explained by severe diffusion limitations in the sediment. Although the Tenax approach has a great deal of potential, it still requires more validation prior to incorporation into sediment risk assessments.

A second approach to estimate bioavailability of HOCs is to use matrix solid phase microextraction (matrix-SPME) [7]. In this technique, SPME fibers, which are coated with a chemical absorbent such as polydimethylsiloxane (PDMS), are directly inserted into the sediment and allowed to come to equilibrium with the sediment-pore water system. At this point, the fibers are removed and directly injected into an analytical instrument to measure the amount of contaminant on the fiber. Only a small fraction of the contaminant in the system will absorb to the fiber resulting in a nondepletive extraction technique that provides a measure of the chemical activity of the contaminant in sediment. The amount of chemical on the fiber then can be related to the concentration in the organism. The SPMEs are often referred to as biomimetic devices, since they can be used as surrogates for organisms to estimate the bioavailability of organic contaminants. To date, no studies have tested and compared Tenax and matrix-SPME approaches using field-contaminated sediment.

The objectives of this study were to compare the Tenax extraction and matrix-SPME approaches to assess the bioavailability of 18 PCB congeners for the oligochaete, *Lumbriculus variegatus*, and determine the influence of the number and positions of substituted chlorines on PCB desorption and bioaccumulation.

MATERIALS AND METHODS

Chemicals

Eighteen PCB congeners and Aroclor 1254 standards (Table 1) were purchased from Ultra Scientific Analytical Solutions

* To whom correspondence may be addressed (mlydy@siu.edu).

Table 1. The polychlorinated biphenyl (PCB) residues detected in sediment collected from Crab Orchard Lake, Williamson County (IL, USA) (C_s, μg/kg total organic carbon [TOC]), PCB residues in *Lumbriculus variegatus* (C_b, μg/kg lipid) after 28 d exposure, and biota-sediment accumulation factors (BSAF, g TOC/g lipid). The PCB data reported as congener and total Aroclor 1254 and values are means ± standard deviation of three replicates. Total organic carbon in sediment was 0.59 ± 0.03% and the lipid content in organism was 1.29 ± 0.05%

Homologue group	PCB[a]	Structure		Log K_{OW}[b]	C_s	C_b	BSAF
Tetra	44	2,2′,3′,5-	2M[c]	5.75	409 ± 70	578 ± 108	1.41 ± 0.36
	49	2,2′,4′,5-	2M	5.85	454 ± 40	887 ± 80	1.95 ± 0.25
	52	2,2′,5,5′-	2M	5.84	1,070 ± 83	1,657 ± 183	1.55 ± 0.21
	66	2,3′,4,4′-	CP1[d]-2M	6.20	739 ± 51	1,248 ± 58	1.69 ± 0.14
	70	2,3′,4′,5-	CP1-2M	6.20	663 ± 44	999 ± 72	1.51 ± 0.15
Penta	87	2,2′,3,4,5′-	2M	6.29	785 ± 44	1,269 ± 70	1.62 ± 0.13
	95	2,2′,3,5′,6-	2M	6.13	1,457 ± 136	2,592 ± 102	1.78 ± 0.18
	97	2,2′,3,4′,5′-	2M	6.29	497 ± 62	866 ± 46	1.74 ± 0.24
	99	2,2′,4,4′,5-	PP[e]	6.39	790 ± 80	1,222 ± 50	1.55 ± 0.17
	101	2,2′,4,5,5′-	2M	6.38	803 ± 90	2,127 ± 318	2.65 ± 0.50
	105[f]	2,3,3′,4,4′-	CP1-PP-2M	6.65	798 ± 65	1,218 ± 61	1.53 ± 0.15
	110	2,3,3′,4′,6-	2M	6.48	2,379 ± 175	4,926 ± 223	2.07 ± 0.18
	118[f]	2,3′,4,4′,5-	CP1-PP-2M	6.74	1,929 ± 196	2,834 ± 135	1.47 ± 0.16
Hexa	128	2,2′,3,3′,4,4′-	PP-2M	6.74	458 ± 75	498 ± 22	1.09 ± 0.18
	138	2,2′,3,4,4′,5-	PP-2M	6.83	2,035 ± 157	2,939 ± 126	1.44 ± 0.13
	153	2,2′,4,4′,5,5′-	PP-2M	6.92	1,689 ± 126	3,076 ± 138	1.82 ± 0.16
	156[f]	2,3,3′,4,4′,5-	CP1-PP-2M	7.18	304 ± 64	343 ± 24	1.13 ± 0.25
Hepta	170	2,2′,3,3′,4,4′,5′-	PP-2M	7.27	245 ± 27	329 ± 29	1.35 ± 0.19
Aroclor 1254[g]					29,153 ± 2,252	49,612 ± 2,208	1.70 ± 0.15

[a] PCB numbering according to the International Union of Pure and Applied Chemistry (IUPAC).
[b] Log K_{OW} values according to Hawker and Connell [14].
[c] 2M = two or more *meta* position (3,3′,5,5′) chlorinated.
[d] CP1 = coplanar (mono-*ortho* planar).
[e] PP = both *para* position (4,4′) chlorinated.
[f] Dioxin-like PCBs.
[g] Aroclor 1254 concentration was calculated from the congener ratio for Aroclor 1254 and further calculation details can be found in the text.

(North Kingstown, RI, USA). Tenax® TA (60–80 mesh), a porous polymer absorbent based on 2,6-diphenylene oxide (Alltech), was used to characterize PCB desorption from sediments. Tenax beads were cleaned prior to use by sonicating three times with 10 ml of acetone:hexane (1:1, v/v) per gram of beads for 5 min with a Branson 3510 Ultrasonic bath (Branson Ultrasonics, Danbury, CT, USA). No PCBs were detected in the blank extracts. Matrix-SPME experiments were conducted with disposable SPME fibers that were coated with 10 μm of PDMS (Fiberguide Industries, Stirling, NJ, USA) and had a phase volume of 0.069 μl per centimeter of fiber. Fiber was cut into 1-cm pieces and washed with methanol and water prior to use. Mercuric chloride ($HgCl_2$) was purchased from Supelco (Bellefonte, PA, USA) and was used to inhibit microbial degradation of the test compounds in sediment during the Tenax extraction and matrix-SPME experiments. Sulfuric acid and copper powder (Fisher Scientific, Pittsburgh, PA, USA) were used to remove lipid and sulfur interferences from the samples. Two surrogate standards, 4,4′-dibromooctafluorobiphenyl (DBOFB) and decachlorobiphenyl (DCBP) were purchased from Supelco and used to verify the performance of the analytical process. All the solvents (pesticide or high performance liquid chromatography [HPLC] grade) were purchased from Fisher Scientific. Moderately hard water (MHW) was prepared following U.S. Environmental Protection Agency (U.S. EPA) methods [8].

Instrumentation

Analysis of PCB congeners was performed on an Agilent 6890 series gas chromatograph equipped with an electron capture detector (GC-ECD) (Agilent Technologies, Palo Alto, CA, USA). Two columns, a HP-5MS and a DB-608 (30 m × 0.25 mm, film thickness 0.25 μm), were used to confirm the analytical results of the sediments, organisms, and Tenax bead extracts. The temperature program for the DB-608 column was set at 100°C, heated to 240°C at 10°C/min, held at 240°C for 2 min, then heated to 280°C at 3°C/min, and held at 280°C for 5.67 min. The temperature program for the HP-5 column was set at 100°C, heated to 180°C at 15°C/min, heated to 200°C at 6°C/min, held at 200°C for 4 min, heated to 220°C at 5°C/min, held at 220°C for 4 min, and heated to 280°C at 3°C/min. Calibration was based on area using five external standards of 1, 5, 10, 50, or 100 μg/L of each PCB congener and surrogate in hexane. The calibration curves were linear within this concentration range. Qualitative identity was established using a retention window of 1% with confirmation on a second column. Surrogate recoveries for sample extraction were 60 to 93%, 73 to 96%, 90 to 127%, and 74 to 120% for sediments, organisms, Tenax beads, and SPME fibers, respectively. Eight PCB congeners (PCB 44, 52, 101, 105, 110, 118, 138, and 153) were selected to quantify the total PCB as Aroclor 1254. The ratio of congener and Aroclor concentration was measured for each congener with standard solutions and used to individually convert the congener concentration to eight Aroclor concentrations. The average Aroclor concentration corresponding to the eight congeners was then calculated and reported as the Aroclor 1254 concentration for the sample.

Sediment

Contaminated sediment was collected from Crab Orchard Lake (IL, USA) in June 2004. Sediment samples were taken using a Wildco Eckman grab sampler (Buffalo, NY, USA) and the sampling location (37°41′39.6960″N, 89°0′49.0680″W) was recorded using a Garmin Geko 201 Global Positioning Satellite unit (Garmin International, Olathe, KS, USA). Approximately 25 kg of sediment was collected, placed in coolers, transported back to Southern Illinois University (Carbondale, IL, USA) and stored at 4°C. Samples were then sieved through a 2-mm sieve in order to remove large debris and native organisms. The sediment was placed in 4-L glass containers, and then homogenized using a Model 47 Scientific Stirrer (Fisher Scientific) equipped with a stainless steel paddle prior to PCB analysis. The PCBs in sediment were quantified with GC-ECD after solvent extraction and sulfuric acid and copper cleanup following the methods previously described [9]. Total organic carbon (TOC) content of the sediment was 0.59 ± 0.03% and was analyzed using an elemental analysis EA1110 carbon–hydrogen–nitrogen analyzer (CE Instruments, Milan, Italy) after removing carbonates with 3 M HCl [10]. The grain size of the sediment was determined by wet sieving and it was composed of 14% sand, 70% silt, and 16% clay [10]. The moisture of sediment was 62.8 ± 0.8%.

Tenax extraction tests

Desorption of PCBs from field-contaminated sediment (duplicate samples) was measured using Tenax extraction following the method of Cornelissen et al. [1]. Two grams of sediment (dry wt), 0.1 g copper, 45 ml MHW, 3 mg $HgCl_2$, and 0.5 g of Tenax beads were added to 50 ml screw-cap centrifuge tubes and the tubes rotated at 20.75 revolutions per minute (rpm) continuously on a tube rotator (JAG Industries, Baltimore, MD, USA). At periodic intervals throughout the experiment (3, 6, 12, 24, 48, 96, 168, 240, and 336 h), Tenax beads were removed from each tube and 0.5 g of fresh beads added into the sediment slurry and rotation restarted. The separation of Tenax beads from the sediment slurry was easily achieved because the beads floated on top of the water, while the sediment particles sank to the bottom of the tubes. The separated Tenax beads were sonicated with 5 ml of acetone and 2 × 5 ml of acetone:hexane (1:1, v/v) for 5 min. The extracts were combined; surrogates (DBOFB and DCBP) were introduced, an additional 10 ml hexane was added, and evaporated until two layers appeared. After removing the upper hexane layer, 2 × 5 ml hexane was added to the water layer to extract any remaining PCBs from the water. The hexane extracts were then combined and evaporated to 1 ml and cleaned with 1 ml of concentrated H_2SO_4. After cleanup, the extract was transferred into a GC vial insert and evaporated to near dryness. Hexane was then added to bring the total volume to 100 μl prior to GC analysis. The efficiency for the Tenax extraction to remove the PCBs from water was determined in a separate experiment by extracting spiked water samples, and recoveries were 93 to 105% for the selected PCB congeners.

Matrix-SPME tests

Matrix-SPME was conducted in triplicate and four time intervals were used for sampling to ensure that equilibrium was achieved between the fiber and sediment. Twelve 20-ml screw-cap glass vials were filled each with 10 g sediment (wet wt), 10 mg $HgCl_2$, 0.5 g copper, and 10 ml overlying MHW. The test was initiated by introducing 10 cm of fiber into a stainless steel mesh envelope. The stainless steel mesh was used to protect the fragile fibers and our previous study [11] showed that the 110 μm openings allowed adequate contact of the fiber with the pore water and sediment particles. The vials were constantly rotated at 125 rpm using a Model G2 Laboratory Rotator (New Brunswick Scientific, New Brunswick, NJ, USA). At each predetermined time point, the mesh envelope was removed from the sediment and rinsed with distilled water. Fibers were removed from the envelope and blotted dry prior to being extracted with 3 × 1 ml of hexane using 10 min of sonication. Extracts were combined, surrogates (DCBP and DBOFB) were added, and extracts were cleaned with 0.75 ml concentrated H_2SO_4 and concentrated to 0.1 ml prior to GC-ECD analysis.

Bioaccumulation test

A 28-d sediment bioaccumulation test was performed in triplicate using field-contaminated sediment with *L. variegatus* following U.S. EPA recommended procedures [8]. *Lumbriculus variegatus* were obtained from a stock culture maintained in the Fisheries and Illinois Aquaculture Center, at Southern Illinois University from cultures originally obtained from the U.S. EPA Environmental Research Laboratory (Duluth, MN). Three replicate 10-L aquaria each received 1 L (wet wt) Crab Orchard sediment and 5 L overlying MHW water. Adult *L. variegatus* (200 individuals per aquaria) were exposed to the sediment after it was allowed to settle for 24 h. To ensure adequate dissolved oxygen concentrations, the overlying water was renewed once daily by the addition of 1 L of MHW and no additional aeration was required. The ratio of sediment TOC to *L. variegatus* was at least 50:1 to minimize possible depletion of contaminants from the sediment. Tests were performed at 23°C with a 16:8 light:dark photoperiod. Dissolved oxygen was monitored daily with a YSI dissolved oxygen meter (Yellow Springs Instruments, Yellow Springs, OH, USA) to ensure concentrations remained above 2.5 mg/L. Overlying water was also monitored for conductivity (~350 μS/cm) and pH (~7.8) using an Oakton multi-meter (Eutech Instruments, Singapore). Food was not provided during the experiments, and the organisms were removed at the end of the exposure by sieving the sediment through a 0.425-mm sieve.

Lumbriculus variegatus were placed in clean water for 6 h of depuration prior to tissue residue analyses. After depuration, the *L. variegatus* were blotted dry and weighed to the nearest 0.1 mg using a Model H18 Balance (Mettler, Hightstown, NJ, USA). Tissue residues were obtained by sonicating the oligochaetes for 20 s in 10 ml of acetone using a Model 501 Sonic Processor (Tekmar, Cincinnati, OH, USA) after spiking with surrogates. After sonication, 10 ml of hexane was then added to each sample, which was shaken and allowed to stand for several hours. The extracts were then sonicated in an ultrasonic water bath for 10 min, evaporated to 1 ml, filtered with anhydrous Na_2SO_4 to remove water and tissue debris, and cleaned with 1 ml of sulfuric acid prior to GC-ECD analysis. Two individuals from each of the three replicate aquaria were used for lipid determinations following the spectrophotometer methods of van Handel [12].

Data analysis

Desorbing fractions and the corresponding rate constants were calculated by fitting the data from the Tenax extraction experiments to a biphasic model [13] using the Scientist 2.01 program (MicroMath Scientific Software, St. Louis, MO, USA).

$$\frac{S_t}{S_0} = F_{\text{rap}} \cdot e^{-k_{\text{rap}} \cdot t} + F_{\text{s}} \cdot e^{-k_{\text{s}} \cdot t} \tag{1}$$

$$F_{\text{rap}} + F_{\text{s}} = 1 \tag{2}$$

where S_t and S_0 represent the amount of sediment-sorbed chemical at time t (h) and time zero, respectively; F_{rap} and F_{s} are the fraction of chemical in the rapidly and slowly desorbing

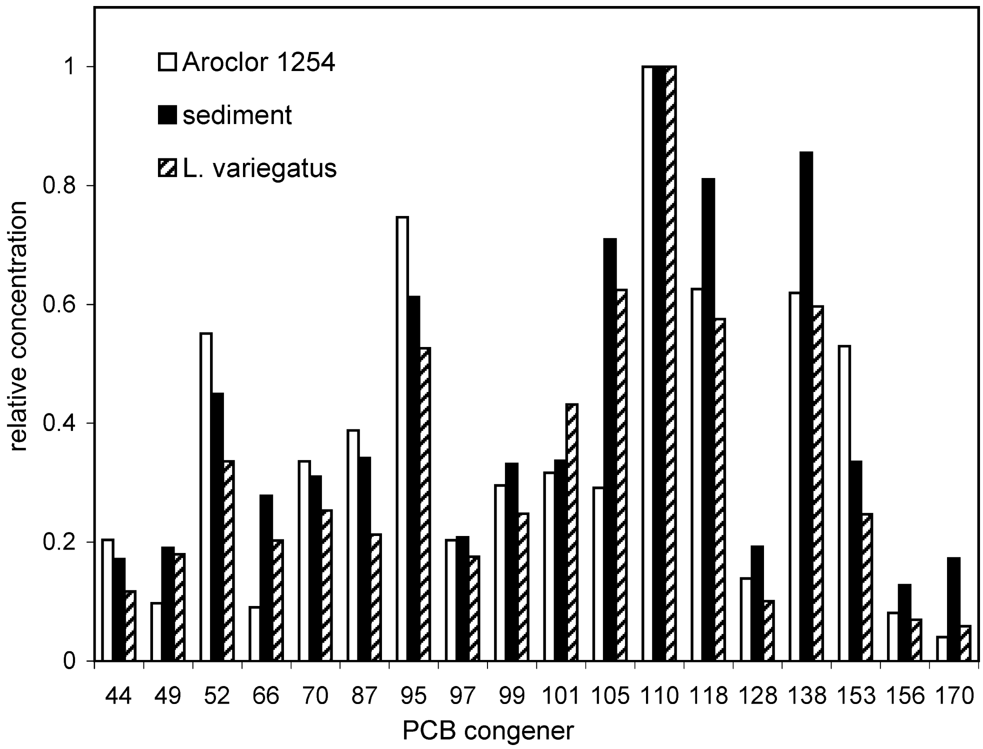

Fig. 1. The polychlorinated biphenyl (PCB) congener composition in an Aroclor 1254 standard, sediment collected from Crab Orchard Lake, Williamson County (IL, USA), and *Lumbriculus variegatus* after a 28-d exposure. Relative concentration is the ratio of concentration of an individual congener to that of PCB 110, which was treated as 1.

compartments at time zero, and k_{rap} and k_s are the corresponding desorption rate constants (h^{-1}). The concentration of PCBs in the rapidly desorbing phase (C_{srap}) was calculated from the following equation.

$$C_{srap} = F_{rap} \cdot C_s \quad (3)$$

where C_s was the organic carbon normalized concentration in sediment.

Similarly, the concentration of PCBs in the rapidly desorbing phase at 6 h (C_{s6h}) was calculated from the following equation.

$$C_{s6h} = F_{6h} \cdot C_s \quad (4)$$

The concentration of PCBs on the matrix-SPME fiber ($C_{f,t}$) at time t (d) was calculated by dividing the mass of compounds on the fiber by the volume of PDMS coating on the fiber. The data was fit to a first-order one-compartment model as follows to estimate the fiber concentration at equilibrium (C_f).

$$C_{f,t} = C_f(1 - e^{-k \cdot t}) \quad (5)$$

where k is the fiber desorption rate constant and was used to predict the time to reach 90% of equilibrium concentration in the fiber.

The freely dissolved concentration of PCBs in pore water (C_{pw}) was derived from C_f at equilibrium and it was used to predict the oligochaete body residues using the following equations.

$$C_{pw} = C_f/K_{fw} \quad (6)$$

$$C_{b,estimated} = C_{pw} \cdot \mathrm{BCF} \quad (7)$$

where K_{fw} and BCF are the fiber and water partition coefficient and the bioconcentration factor (lipid normalized) and C_b is the lipid normalized organism concentration. The lipid content for the oligochaetes was 1.29 ± 0.05% on a wet weight basis. The K_{fw} and BCF values were estimated using K_{OW} values of selected PCB congeners [14] from the following regression equations: $\log K_{fw} = \log K_{OW} - 0.91$ [15] and $\mathrm{BCF} = 1.01 \log K_{OW} - 0.07$ [16].

Bioavailability of the HOC from sediment was expressed as a BSAF value and was calculated as follows:

$$\mathrm{BSAF} = \frac{C_b \text{ (normalized to lipid)}}{C_s \text{ (normalized to organic carbon)}} \quad (8)$$

where C_b was the lipid-normalized concentration in *L. variegatus*; therefore, the units for BSAF are grams of sediment TOC per grams of organism lipids. Note that traditional BSAF calculations assume that all of the contaminant in the sediment is equally available. Pretest concentrations were used for all calculations, because no significant change (<15%) in sediment PCB concentrations occurred during the test.

RESULTS

Polychlorinated biphenyls in field-contaminated sediment

The elevated PCB concentrations detected in the Crab Orchard sediment had a congener pattern similar to that of Aroclor 1254, although some weathering of the pattern was noted (Fig. 1). The weathering occurred mostly for the lower chlorinated congeners. Sixteen PCB congeners were detected at greater than 5 μg/kg dry weight including five tetra-PCBs (44, 49, 52, 66, and 70), eight penta-PCBs (87, 95, 97, 99, 101, 105, 110, and 118), and three hexa-PCBs (128, 138, and 153). Two additional congeners detected at lower concentrations, PCB156 and PCB170, were also used in this study (Table 1). The PCB156 congener was included because of its dioxin-like structure, while PCB170 was the only hepta-PCB detected. The 18 PCBs represent over 90% of Aroclor 1254 mass and

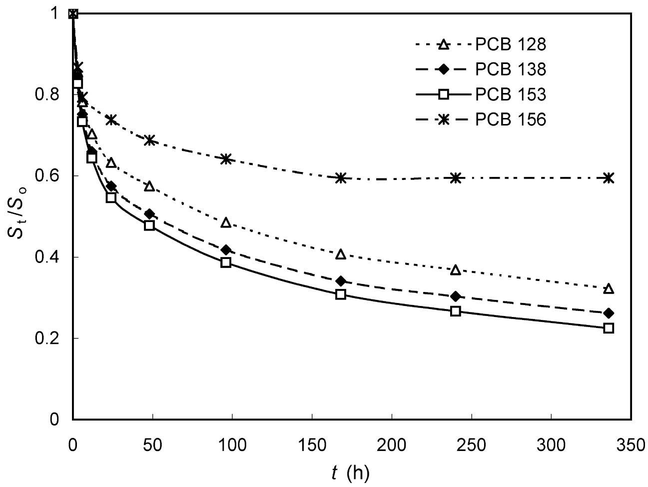

Fig. 2. Desorption of hexa-polychlorinated biphenyls (PCBs) (PCB 128, 138, 153, and 156) from sediment collected from Crab Orchard Lake, in Williamson County (IL, USA) modeled using a biphasic model. S_t and S_0 represent the amount of sediment-sorbed chemical at time t (h) and time zero, respectively.

consisted of planar and nonplanar PCBs. Among the five planar PCBs (66, 70, 105, 118, and 156), PCBs 105, 118, and 156 should be the most toxic due to their dioxin-like structures [17].

Bioaccumulation test

Average survival rates for *L. variegatus* during the tests were 106 ± 6%, and no overt avoidance of the sediment was observed during the exposure. The BSAF values calculated for each PCB congener and total PCB as Aroclor 1254 are listed in Table 1, and ranged from 1.1 to 2.6 g TOC/g lipid for the 18 PCB congeners and 1.7 g TOC/g lipid for Aroclor 1254.

Tenax extraction

A biphasic kinetic model was used to describe desorption of the PCBs from the sediment, and it fit our data very well with coefficient of determinations ($r^2 > 0.98$) and relatively small standard deviations across all PCB congeners (Fig. 2 and Table 2). A single point Tenax extraction at 6 h was compared with the full-scale consecutive Tenax extraction and the average ratio of F_{rap}/F_{6h} was 1.62 ± 0.14. Differences in the rapidly desorbing fraction or the fraction desorbed within 6 h accounted for 39% and 31% of the difference among BSAF values with regression equations of log BSAF = 0.92 (0.29) F_{rap} − 0.17 (0.12) and log BSAF = 1.28 (0.48) F_{6h} − 0.12 (0.12), respectively. The slope and intercept were expressed as means (± standard deviation) for the regression lines. However better relationships were found between the PCB residues in *L. variegatus* (C_b) and the concentration in the rapidly desorbing fraction (C_{srap}) (C_b = 4.11 [0.25] C_{srap} − 24.5 [124], r^2 = 0.94) and the concentration in the fraction desorbing in 6 h (C_{s6h}) (C_b = 6.94 [0.39] C_{s6h} − 68.2 [117], r^2 = 0.95) (Fig. 3).

Matrix-SPME

The PCB concentrations, with the exception of PCB156, reached 90% of equilibrium between the fiber and sediment in 12 to 38 d using a 10-μm fiber coating. A first-order one-compartment model (see Eqn. 5) was used to estimate C_f at equilibrium, which was compared to the PCB residues in *L. variegatus* after exposure to Crab Orchard Lake sediment (Fig. 4). A good relationship was found between PCB residues on the fiber and *L. variegatus* concentrations (C_b = 7.96 [0.75] C_f −172 [200], r^2= 0.88). The concentration in the pore water (C_{pw}, Table 3) calculated from C_f and K_{fw} was used to predict the oligochaete body residue using literature BCF values [16]. Results showed that the matrix-SPME could predict the oligochaete body residues in the range of 0.4 to 1.3 as the ratio of C_b measured/C_b predicted (Table 3). The regression between

Table 2. Desorption parameters and standard deviation of polychlorinated biphenyls (PCBs) congeners from sediment collected from Crab Orchard Lake, Williamson County (IL, USA) (n = 2). Rapidly and slowly desorbing fractions (F_{rap} and F_s) and their corresponding rapid and slow desorption rate constants (k_{rap} and k_s). Data were fitted with a biphasic kinetic model with Scientist Version 2.01 (1995; MicroMath Scientific Software, St. Louis, MO, USA)

PCB[a]	Kinetic parameter[b]				
	F_{rap}	k_{rap} (h^{-1})	F_s	k_s (h^{-1})	r^2
44	0.3596 ± 0.0656	0.1253 ± 0.0522	0.6205 ± 0.0547	0.0036 ± 0.0007	0.9765
49	0.4636 ± 0.0293	0.1405 ± 0.0205	0.5202 ± 0.0226	0.0026 ± 0.0031	0.9941
52	0.4694 ± 0.0242	0.1109 ± 0.0128	0.5167 ± 0.0215	0.0043 ± 0.0003	0.9978
66	0.3581 ± 0.0310	0.1354 ± 0.0275	0.6233 ± 0.0229	0.0015 ± 0.0002	0.9880
70	0.4376 ± 0.0247	0.1107 ± 0.0143	0.5480 ± 0.0212	0.0033 ± 0.0003	0.9969
87	0.4503 ± 0.0255	0.1327 ± 0.0170	0.5384 ± 0.0212	0.0040 ± 0.0003	0.9969
95	0.4313 ± 0.0173	0.1203 ± 0.0109	0.5610 ± 0.0149	0.0040 ± 0.0002	0.9987
97	0.4858 ± 0.0315	0.1725 ± 0.0257	0.5058 ± 0.0225	0.0025 ± 0.0003	0.9924
99	0.4331 ± 0.0243	0.1352 ± 0.0175	0.5539 ± 0.0193	0.0030 ± 0.0003	0.9963
101	0.4313 ± 0.0269	0.1208 ± 0.0176	0.5586 ± 0.0218	0.0026 ± 0.0003	0.9951
105	0.3248 ± 0.0242	0.1197 ± 0.0212	0.6626 ± 0.0186	0.0014 ± 0.0002	0.9922
110	0.4580 ± 0.0284	0.1329 ± 0.0188	0.5284 ± 0.0233	0.0037 ± 0.0004	0.9959
118	0.3627 ± 0.0279	0.1192 ± 0.0215	0.6237 ± 0.0221	0.0020 ± 0.0002	0.9929
128	0.3598 ± 0.0268	0.1260 ± 0.0219	0.6294 ± 0.0211	0.0022 ± 0.0002	0.9938
138	0.4251 ± 0.0271	0.1192 ± 0.0177	0.5640 ± 0.0221	0.0026 ± 0.0003	0.9951
153	0.4422 ± 0.0283	0.1245 ± 0.0184	0.5452 ± 0.0231	0.0030 ± 0.0003	0.9952
156	0.2528 ± 0.0179	0.2501 ± 0.0377	0.7478 ± 0.0129	0.0014 ± 0.0002	0.9956
170	0.3613 ± 0.0295	0.0941 ± 0.0181	0.6258 ± 0.0254	0.0021 ± 0.0002	0.9932

[a] PCB numbering according to the International Union of Pure and Applied Chemistry (IUPAC).
[b] r^2 = coefficient of determination.

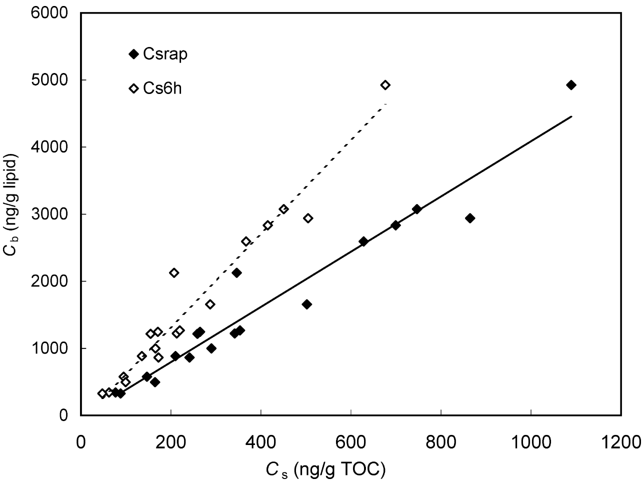

Fig. 3. Relationship between the polychlorinated biphenyl (PCB) body residues in *Lumbriculus variegatus* (C_b) and the rapidly desorbing sediment concentration (C_{srap}) corresponding to the rapidly desorbing fraction (F_{rap}) or sediment concentration desorbing within 6 h (C_{s6h}) corresponding to the fraction desorbing within 6 h (F_{6h}). Dark diamonds represent data for C_{srap} ($C_b = 4.11$ [0.25] $C_{srap} - 24.5$ [124], $r^2 = 0.94$) and the open diamonds represent data for C_{s6h} ($C_b = 6.94$ [0.39] $C_{s6h} - 68.2$ [117], $r^2 = 0.95$). TOC = total organic carbon (OC) and the regression equations are expressed as y = slope (± standard deviation) x + intercept (± standard deviation).

the measured and estimated values was $C_{b,measured} = 0.99$ (0.09) $C_{b,estimated} - 177$ (197), $r^2 = 0.88$.

Influence of PCB structure on desorption and bioaccumulation processes

Variations in desorption and bioaccumulation processes were observed among the PCB congeners that differed in the numbers and positions of substituted chlorines on the biphenyl rings (Fig. 5). The log BSAF values for PCBs in *L. variegatus* significantly decreased with increasing numbers of substituted chlorines from 0.232 ± 0.016 to 0.127 ± 0.029 g TOC/g lipid. Further, the log BSAF values were also significantly greater for the nonplanar PCBs (0.219 ± 0.017) compared to the planar PCBs (0.162 ± 0.026). The preferential bioaccumulation of the lower chlorinated and nonplanar PCBs was mimicked by the significantly different desorption behaviors (F_{rap}) among PCB structures (Fig. 5).

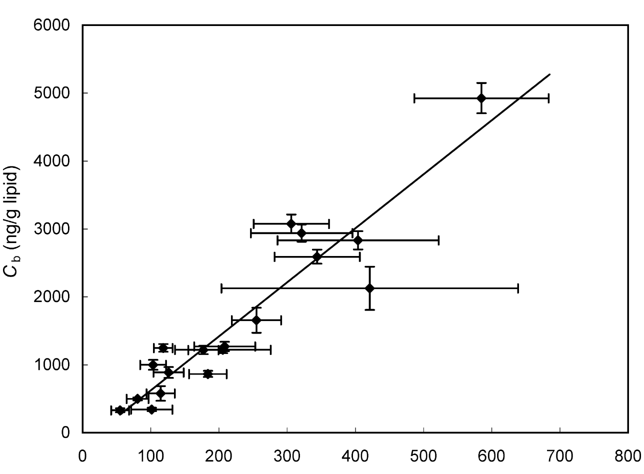

Fig. 4. Relationship between the polychlorinated biphenyl (PCB) body residues in *Lumbriculus variegatus* (C_b) and solid phase microextraction fiber (C_f) exposed to a field-contaminated sediment from Crab Orchard Lake, Williamson County (IL, USA) ($C_b = 35.8$ [7.24] $C_f + 234$ [340], $r^2 = 0.60$). The error bars represent standard deviation. PDMS = polydimethylsiloxane and the regression equations are expressed as y = slope (± standard deviation) x + intercept (± standard deviation).

Table 3. The calculated freely dissolved polychlorinated biphenyl (PCB) concentration in pore water (C_{pw}), estimated PCB residues in *Lumbriculus variegatus* ($C_{b,estimated}$) determined by matrix solid phase microextraction (matrix-SPME), and the ratio of measured PCB residues in *L. variegatus* determined by bioaccumulation test ($C_{b,measured}$, from Table 1) to estimated PCB residues in *L. variegatus* determined by matrix-SPME. The PCB data are reported as congeners and values are means ± standard deviation of three replicates

PCB[a]	C_{pw} (pg/L)	$C_{b,estimated}$ (μg/kg lipid)	Ratio
44	1,655 ± 299	905 ± 164	0.64 ± 0.16
49	1,449 ± 255	999 ± 176	0.89 ± 0.17
52	2,997 ± 424	2,109 ± 286	0.82 ± 0.14
66	607 ± 70	945 ± 109	1.32 ± 0.16
70	531 ± 97	826 ± 151	1.21 ± 0.23
87	869 ± 187	1,667 ± 358	0.76 ± 0.17
95	2,072 ± 377	2,740 ± 498	0.95 ± 0.17
97	767 ± 115	1,470 ± 220	0.59 ± 0.09
99	681 ± 233	1,649 ± 564	0.74 ± 0.25
101	1,427 ± 736	1,429 ± 179	0.85 ± 0.11
105	322 ± 40	3,375 ± 1,741	0.63 ± 0.34
110	1,574 ± 265	4,698 ± 792	1.05 ± 0.18
118	598 ± 175	3,264 ± 955	0.87 ± 0.26
128	119 ± 24	652 ± 129	0.76 ± 0.15
138	386 ± 90	2,601 ± 603	1.13 ± 0.26
153	299 ± 54	2,483 ± 448	1.24 ± 0.23
156	54 ± 16	827 ± 247	0.41 ± 0.13
170	24 ± 6	451 ± 107	0.73 ± 0.18

[a] PCB numbering according to the International Union of Pure and Applied Chemistry (IUPAC).

DISCUSSION

The ability to predict the bioavailability of sediment-associated nonpolar contaminants was improved by the formulation of the equilibrium partitioning theory [18]. More recent work, however, has shown considerable variability in BSAF values for a given compound that can vary by as much as a factor of 10 [19]. The reason for this variability becomes evident when considering the fraction of contaminant that is available for bioaccumulation. The fraction available appears to vary among sediments and this variation does not simply correspond to the amount of TOC in the given sediment, but the composition of the organic carbon as well [20]. This is exemplified by the recent finding that black carbon composed of soots, chars, charcoal, cenospheres, and coke was a major contributor to partitioning behavior of contaminants in sediments [21]. Therefore, the ability to predict partitioning and thus bioavailability from sediment components remains an issue [20]. For the near future, methods that can identify a contaminant's chemical activity in the sediment matrix will be the mainstay for predicting the bioavailability of sediment-associated contaminants. The two methods used in the present study are expected to serve as measures of bioavailability of nonpolar contaminants in sediments. The two methods examine, however the sediment-pore water–organism interaction from different points of view. The Tenax approach defines the bioaccessible fraction as that which readily desorbs from sediment, so it is essentially a measure of the active component of the sediment concentration, while the matrix-SPME essen-

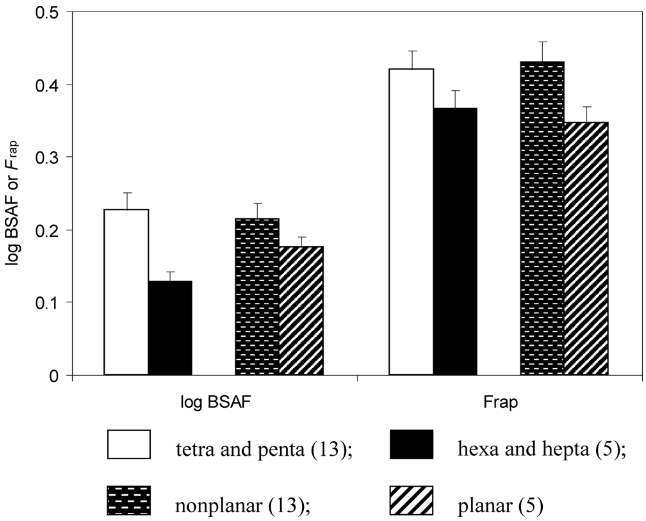

Figure 5. Variation in average biota-sediment accumulation factors (log BSAF) for *Lumbriculus variegatus* and average rapid desorbing fraction (F_{rap}) among tetra-, penta-, hexa-, and hepta-polychlorinated biphenyl (PCBs) and nonplanar and planar PCBs. The numbers after each legend represent the number of PCB congeners within each group. Error bar represent the standard error (n = 3 for BSAF and n = 2 for F_{rap}).

tially mimics the pore water concentration by measuring the concentration that is in equilibrium with sediment. So while the focus of the two approaches are on two different phases, sediment versus pore water, refinement of equilibrium partitioning theory for the bioavailable fraction would need to reflect the rapidly desorbed sediment fraction in equilibrium with the pore water and organism [16].

Tenax extraction

Recent studies have shown that desorption of organic chemicals from sediment occurs from multiple compartments and the corresponding desorption rates from these compartments vary by several orders of magnitude [1,22]. Though it is impossible to qualify how many compartments exist within a given sediment, empirical models have been developed to describe the desorption process [1,5]. While both biphasic and triphasic kinetic models have been used to describe desorption, the biphasic model fit our PCB data better with overall greater $r^2 > 0.98$ and smaller standard deviations across all PCB congeners (Fig. 2 and Table 2). The use of a biphasic model contrasts with results noted in previous studies that used a triphasic model to describe desorption of HOCs from laboratory-spiked sediments [6,22]. The apparent absence of a third desorbing fraction in the field-contaminated sediments may have resulted from the overall slower desorption rates of aged field contaminants compared to laboratory spiked contaminants (Fig. 2). The presence of two phases is consistent, however, with descriptions of the degradable fractions of PAHs in sediments [23]. The biphasic model used to fit our data describes two compartments including F_{rap}, where chemicals are readily reversibly sorbed and can be described by linear isotherms, and F_s, where desorption of the chemicals was hindered. F_{rap}, with a k_{rap} of approximately 0.1 h^{-1}, is suggested as the contaminant pool that is bioavailable and contributes to bioaccumulation, while F_s, with a k_s of approximately 10^{-3} h^{-1} would contribute substantially less to the bioaccumulation process [3,6,24,25].

A single point Tenax extraction at 6 h is a simple and rapid substitute for the full-scale consecutive Tenax extraction [2,4], and the average ratio of F_{rap}/F_{6h} was 1.62 ± 0.14, which is smaller, but similar to the ratio of 2.04 found by Cornelissen et al. [2]. However, Kukkonen et al. [5] suggested that a 6-h desorption measure was not as useful for tracking F_{rap} as a 24-h measure. Further, Shor et al. [23] also found a 24-h extraction was representative of F_{rap} for PAH from field-collected sediment. Both 6-h and 24-h time points have been used as surrogates for F_{rap} with success [4,23]. The success of such surrogates assumes that the shorter measurement reflects a proportion of F_{rap}. However in cases where the desorption rates are slower, a 6-h measure may underrepresent more strongly sorbed compounds such as benzo[*a*]pyrene. At this time, it is not possible to definitively determine which length of desorption would serve as a better surrogate.

Both F_{rap} and F_{6h}, measured with Tenax extraction, correlated equally well with the BSAF of PCBs in the sediments with r^2 values of 0.39 and 0.31, respectively. The relationship between F_{rap} and log BSAF was better than that between F_{rap} and BSAF and this is consistent with Kukkonen et al. [5]. However, the equation relating F_{rap} and log BSAF was still not very strong and was substantially different between our current study, and that of Kukkonen et al. [5] which may be due in part to the difference between a laboratory-spiked sediment and a field-contaminated sediment. The F_{6h} estimate provided a prediction of log BSAF that was comparable to F_{rap} that follows the work of Cornelissen et al. [2].

A question remains, however whether a comparison between F_{rap} and BSAF is appropriate. The BSAF calculation includes contributions from the slowly desorbing fraction of chemical in sediment as part of the denominator in the equation. Thus, the relationship between F_{rap} and BSAF is not a direct comparison between the expected fraction available for bioaccumulation from sediment and that accumulated by the organism. A cleaner comparison can be made between the concentration of chemical in the biota (C_b) and the concentration of chemical in the rapidly desorbing fraction (C_{srap}) of the sediment as shown in Equation 3. This leads to a very strong correlation and a clear indication that F_{rap} is in fact a major fraction contribution to bioavailability (Fig. 3).

Both C_{srap} and C_{s6h} provide strong correlations with C_b and the intercepts are not significantly different from zero indicating a constant relationship between the amount of chemical bioavailable in the sediment and the amount of chemical bioaccumulated in the organism. The difference in the slope between the two lines suggests the reduced proportion of the rapidly desorbing fraction represented by F_{6h} compared to F_{rap}. The slope of 4.11 for the C_b versus C_{srap} relationship suggests that the lipid in the organism has four times more capacity for the chemicals than the fraction of organic matter in the sediment contributing to the bioaccumulation. The regression between C_b and C_{s6h} was similar to that found for oligochaetes [4], and the slope (e.g., 6.94) falls in the mid range for sediments of varying organic carbon composition. Thus, difficulties remain for accurately predicting bioavailability across sediments even after accounting for F_{rap} because the slopes of the regressions lines, though strong for each sediment, continue to vary between 2 and 9 for various sediments [4]. Although the variability in predicting bioavailability decreases with the Tenax approach compared to equilibrium partitioning theory, it appears that other as yet unidentified factors will be needed to improve the prediction across sediments, such as different digestive mechanisms and selective feeding behaviors of organisms [26].

Matrix-SPME

The matrix-SPME method has been successfully used to predict bioavailability for laboratory-spiked sediments [16,27,28], however only a few studies [29,30] have examined field-contaminated soils. Van der Wal et al. [29] tested the possibility of matrix-SPME to act as a surrogate for HOC accumulation in earthworms in field-contaminated soils, and found that earthworm concentrations were correlated to the fiber concentrations.

In the current study, PCB concentrations in the matrix-SPME fiber at equilibrium were compared to PCB residues in *L. variegatus* after exposure to Crab Orchard Lake sediment (Fig. 4). A good relationship was found between PCB residues on the fiber and *L. variegatus* concentration for aged PCBs (C_b = 7.96 [0.75] C_f − 172 [200], r^2= 0.88). With a slope of 7.96 and an intercept not significantly different from zero, oligochaetes demonstrated much greater accumulation than measured in the PDMS fibers. This is consistent with the predicted relative capacity of the lipid that is approximately seven times that of the PDMS for HOCs (C_b/C_f = 6.9, and ranged from 2.4 to 20) based on the relationships between BCF, K_{fw}, and K_{OW} [15,16].

Along with the literature K_{fw} and BCF values, C_f was used to calculate the freely dissolved PCB concentration in sediment pore water and in turn, body residues in *L. variegatus*. At sediment concentrations of 1.4 to 14.0 μg/kg dry weight, C_{pw} ranged from 24 to 2072 pg/L and predicted oligochaete body residues were 5.8 to 60.6 μg/kg wet weight (Table 3). Comparison of the estimated and measured body residues in *L. variegatus* determined by matrix-SPME supported the application of the SPME fiber as a biomimetic sampler. The ratio of the measured and calculated bioaccumulation factors were between 0.4 and 1.3 with an average of 0.87 ± 0.05 (Table 3) for a relatively low PCB field-contaminated sample.

Influence of PCB structure on desorption and bioaccumulation processes

Variations in desorption and bioaccumulation processes were observed among the PCB congeners that differed in the numbers and positions of substituted chlorines on the biphenyl rings (Fig. 5). Increased hydrophobicity and larger molecular volumes may be the causes for the decrease in desorption and bioaccumulation with an increase in the numbers of substituted chlorines. Bucheli and Gustafsson [31] reported a strong interaction of planar PCBs with planar soot in sediment and this might be the explanation for the higher sequestration of planar PCBs and lower bioaccumulation observed in this study. The effects of HOC planarity on sorption to carbonaceous geosorbents have recently been reviewed [21]. In that review, Cornelissen et al. [21] suggested that strong sorption of planar HOC could account for the lower BSAF values for the planar PAHs compared to nonplanar PCBs supporting our similar finding. The greater abundance of congeners with a lower degree of chlorination in rapidly desorbing fractions may also help to explain their higher weathering rates in sediment and the shift in the congener distribution (Fig. 1).

Overall, both chemical approaches, namely Tenax extraction and matrix-SPME, could serve as low-cost and simple predictive tools to measure bioavailability in field-contaminated sediment. However, the two techniques track the bioavailability from different perspectives [32]. Matrix-SPME measures the chemical activity at equilibrium and could provide direct estimation of organism body residues, therefore, this technique is preferred. Our calculated BSAF values were similar to those predicted from equilibrium partitioning theory yielding an Aroclor 1254 BSAF of 1.7 [33]. However, variation among bioavailability among PCB congeners was observed. The effects of chlorination and planarity on PCB bioavailability were attributed to their different chemical availability. The fact that equilibrium partitioning theory works fairly well for this sediment simply suggests that the relative bioavailability between the sediments used for the present study and those used for developing the equilibrium partitioning theory were similar, but does not suggest that this result would occur if different sediments were used. What is expected is that there should be equilibrium between the rapidly desorbed sediment-associated contaminant, the pore water, and the organism. Therefore, BSAF may not be the best term to describe bioavailability of sediment-associated organic contaminants and the correction suggested by Kraaij et al. [16] to correct for the fraction rapidly desorbing may provide a more predictive approach.

Acknowledgement—The authors thank Duane Gossiaux for conducting of sediment organic carbon analyses, Fiberguide Industries for providing the disposable SPME fibers, and Jon Maul and the reviewers for their reviews of the paper. Great Lakes Environmental Research Laboratory (GLERL) Contribution 1422.

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